ethereal suspension was stirred for one hour, and then filtered. The solid was treated with water to evolve ammonia and produce an oil from which there was isolated 8 g. (77%) of benzophenone, b.p. 166–167° at 8 mm., identified as its 2,4-dinitrophenylhydrazone. The ethereal filtrate was evaporated, and the residue was distilled to give 6.03 g. (80%) of benzyl chloride, b.p. 67–69° at 20 mm., and 9.5 g. (94%) of diphenylmethane, b.p. 121–123° at 10 mm.

The gray precipitate of adduct III was prepared again and the diphenylmethane then added as described above. The ammonia was removed and the resulting ethereal suspension was filtered. A portion of the solid was hydrolyzed to give ammonia and benzophenone, isolated as its oxime, m.p. 143–144°. Another portion of the solid was heated in toluene for 3 hours to give benzamide, m.p. and mixed m.p. 127–128°, and a relatively small amount of benzoic acid, m.p. 121°.

Base-catalyzed Cleavage of Carbinol I. (A) With Sodium Amide.—Eight grams of 1,1,2,2-tetraphenylethanol (I) was added to 10 mole per cent. of sodium amide in 200 ml. of liquid ammonia and 50 ml. of ether. The liquid ammonia was allowed to reflux under a Dry Ice–acetone condenser until all of the solid had dissolved (about 2 hr.). The reaction mixture was poured into excess of ammonium chloride in liquid ammonia. The ammonia was removed, and ether and water were added. The ethereal layer was combined with an ether extract of the aqueous layer. The ethereal solution was dried over Drierite, and the solvent removed. The oily residue was treated with 2,4-dinitrophenylhydrazine reagent, and the resulting precipitate of the 2,4-dinitrophenylhydrazone of benzophenone was removed. The yield was 95%. From the filtrate there was isolated an 87% yield of diphenylmethane, b.p. 116–123° at 10 mm. No unreacted carbinol I was recovered.

(B) With Sodium Ethoxide.—To 100 ml. of absolute ethanol containing 50 ml. of tetrahydrofuran was added 0.12 g. of sodium metal. When the metal had dissolved, 17.5 g. (0.05 mole) of carbinol I was added and the mixture was refluxed in a system protected from atmospheric moisture by a drying tube. All the solid did not dissolve even in the boiling solution. Overnight heating gave a homogeneous solution. Glacial acetic acid (1 ml.) was added to the solution and the solvent was evaporated on the steam-bath under aspirator vacuum to a volume of about 25 ml. The solution was treated with 2,4-dinitrophenylhydrazine reagent and the resulting precipitate of the 2,4-dinitrophenylhydrazone of benzophenone, m.p. 238–239°, was removed. The yield was 95%. From the filtrate there was isolated a 72% yield of diphenylmethane, b.p. 119–121° at 10 mm. No unreacted carbinol was recovered.

DURHAM, N. C.

COMMUNICATIONS TO THE EDITOR

DIFFUSION COEFFICIENTS OF H_2O-D_2O MIXTURES

Sir:

Adamson and Irani[1] measured the diffusion coefficients of liquid H_2O–D_2O mixtures and found a pronounced minimum at roughly equimolal composition. This curious behavior, which was *not* observed for H_2O^{18} trace diffusion, implies strange limitations on the mechanism of proton migration in water, and it seemed important to reinvestigate the problem by a different technique. Using the porous-frit method,[2,3,4] we have obtained the results given in Table I. The diffusion coefficients are in good agreement with earlier observations (see reference 1) made at low deuterium concentrations, but show little composition dependence.

TABLE I

DIFFUSION COEFFICIENTS OF H_2O–D_2O MIXTURES AT 25.0 ± 0.4°

$c_i{}^a$	$c_o{}^b$	$D \times 10^5$, cm.^{2} sec.$^{-1}$
24	0	2.29
60	24	2.32
55	35	2.20
100	0	2.26

^{a} Initial weight % D_2O inside frit. ^{b} Initial weight % D_2O outside frit.

An unglazed Selas frit was used in all runs and was calibrated with aqueous potassium chloride. To determine whether we could detect significant variations of D with composition, several experiments were made with concentrated calcium chloride solutions. These results and the calibrations with potassium chloride are summarized in Table II, where the subscripts i and o refer to the solutions inside and outside the frit, respectively. The values of D_i and D_o are those of Lyons and Riley[5] for calcium chloride and of Gosting[6] for potassium chloride. The last column gives the diffusion constants found in our experiments.

TABLE II

DIFFUSION COEFFICIENTS OF AQUEOUS SALT SOLUTIONS AT 25°

Salt	$c_i{}^a$	$c_o{}^a$	$D_i \times 10^5$	$D_o \times 10^5$	$D_{obs} \times 10^5$
KCl	2.0	1.0	2.00	1.89	$(1.91)^b$
	2.5	0	2.06	1.93	1.94
$CaCl_2$	6	2	0.40	1.31	1.34
	4	2	1.08	1.31	1.35
	6	4	0.40	1.08	0.87
	2	4	1.31	1.08	1.29
	2	6	1.31	0.40	0.78
	4	6	1.08	0.40	0.74

^{a} Salt concentrations in moles liter^{-1}. ^{b} Value assumed for calibration.

For the first two calcium chloride runs, the observed D is close to that for the outside solution, as suggested by Wall and Wendt[7] and by Wagner[8]; but for the others it is closer to the mean of D_i and D_o. Convection is a possible source of error.[9] However, the density differences between inside and outside solution in the calcium chloride runs were greater than for the experiments of Table I.

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[1] A. W. Adamson and R. R. Irani, THIS JOURNAL, **79**, 2967 (1957).

[2] F. T. Wall, P. F. Grieger and C. W. Childers, *ibid.*, **74**, 3562 (1952).

[3] G. B. Taylor and F. T. Wall, *ibid.*, **75**, 6340 (1953).

[4] F. Grün and C. Blatter, *ibid.*, **80**, 3838 (1958).

[5] P. A. Lyons and J. F. Riley, *ibid.*, **76**, 5216 (1954).

[6] L. J. Gosting, *ibid.*, **72**, 4418 (1950).

[7] F. T. Wall and R. G. Wendt, *J. Phys. Chem.*, **62**, 1581 (1958).

[8] C. Wagner, *Trans. AIME*, **44**, 91 (1952).

[9] R. H. Stokes, THIS JOURNAL, **72**, 763 (1950).

Therefore, convection cannot cause the observed values of D in the H_2O–D_2O experiments to stray appreciably outside the range from D_i to D_o. Thus we would have observed easily the enormous decrease of D reported by Adamson and Irani, and we must conclude that their measurements are erroneous.

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RECEIVED MARCH 6, 1959

THE PREPARATION OF A CRYSTALLINE gem-DITHIOL UNDER MILD CONDITIONS

Sir:

We wish to report the synthesis in 80% yield of the first crystalline *gem*-dithiol, 2,2-dimercapto-1,3-diphenylpropane, m.p. 81.5–83°, by the combined action of hydrogen sulfide and hydrogen chloride upon dibenzyl ketone at atmospheric pressure. Since these conditions heretofore have been used for the preparation of thioketones and thioaldehydes (or their polymers) in variable yield,[1] we believe that previous investigators have failed to recognize that *gem*-dithiols are among the reaction products because the reaction mixtures have been worked up by the use of procedures which would have destroyed *gem*-dithiols. It seems likely that the formation of *gem*-dithiols from carbonyl compounds is of far greater generality than has been recognized up to the present time, and that their presence can explain some puzzling reaction products which have been observed. We are exploring the scope of the reaction, as well as the chemistry of *gem*-dithiols, broadly. The first previous synthesis[2] of *gem*-dithiols utilized pressures in the range of 35–8500 atmospheres without added catalysts, and yields were commonly 15 to 35%.

A solution of dibenzyl ketone (19.4 g., 0.0924 mole) in 50 ml. of ethanol was cooled in an ice-bath. Dry hydrogen chloride and dry hydrogen sulfide were simultaneously bubbled through the solution for a period of six hours. The reaction mixture was allowed to stand overnight in a refrigerator. The precipitate was filtered, washed with cold ethanol, and dried in air to yield 19.6 g. (80%) of colorless, granular crystals, m.p. 75–80°. Two recrystallizations from ethanol (at temperatures not exceeding 50°) yielded 15 g. of colorless needles, m.p. 81.5–83°. Infrared absorption at 2570 cm.$^{-1}$ showed the presence of the sulfhydryl group; carbonyl absorption was absent. Sodium nitroprusside gave a positive sulfhydryl test. Lead acetate produced a yellow precipitate which slowly turned black on standing, a behavior typical of *gem*-dithiols.[2] *Anal.* Calcd. for $C_{15}H_{16}S_2$: C, 69.18; H, 6.19; S, 24.63. Found: C, 69.41; H, 6.31; S, 24.63.

The *gem*-dithiol yielded with 2,4-dinitrophenylhydrazine reagent the same orange crystalline 2,4-dinitrophenylhydrazone as dibenzyl ketone, m.p. 98.5–99.5° after recrystallization from ethanol. Identification was made by comparison of melting points (no depression on admixture) and infrared absorption spectra.

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[1] (a) A. Schönberg, p. 705 ff., in "Methoden der organischen Chemie," (Houben-Weyl), 4th ed. (ed. E. Müller), G. Thieme, Stuttgart, Vol. 9, 1955; (b) E. Campaigne, *Chem. Rev.*, **39**, 1 (1946).

[2] T. L. Cairns, G. L. Evans, A. W. Larcher and B. C. McKusick, THIS JOURNAL, **74**, 3982 (1952).

EXCHANGE RATES OF ACETYLENIC HYDROGENS IN AQUEOUS SOLUTIONS[1]

Sir:

Available studies on the exchange of acetylenic hydrogens with those of aqueous solutions do not establish definitely the details of the exchange process but do imply that the rate is only moderate, even when the aqueous phase contains one molar hydroxide ion.[2,3] In view of the acidic character of acetylenes,[4,5] this is surprisingly slow. We have consequently reinvestigated this exchange for phenylacetylene and for acetylene itself. For the first of these, $C_6H_5C_2D$ was prepared and aliquots were shaken with aqueous buffer solutions at 25°. Analysis was made with an infrared spectrometer on solutions of the phenylacetylene in carbon tetrachloride. In the second case, acetylene was shaken at 25° with buffers made up with water which contained 60 atom per cent. deuterium. Analysis of the C_2HD formed was made by gas phase infrared. In both cases the aqueous hydrogens were in large excess and only initial rates were measured so that reverse processes can be neglected. At *p*H values below ten the rate of exchange easily could be made independent of the degree of shaking, indicating that the slow step occurred in the aqueous phase. We therefore have used the observed half-times for exchange and the measured mole ratios and solubilities to calculate the listed values of the first order rate coefficients for the solution reaction. The relevant equation is $k_{\text{soln}} = 0.69A/V_BSt_{1/2}$, where A is total moles and S is aqueous solubility of the acetylene compound, V_B is volume of aqueous phase and $t_{1/2}$ is the observed half-time for the two-phase exchange.

Solution	*p*H	$10^6k_{\text{soln.}}$, sec.$^{-1}$
Acetylene		
0.02 M total phosphate	8.60	2600
0.02 M total phosphate	9.04	6000
Phenylacetylene		
0.01 M HCl	2	no exchn.
0.04 M total acetate	5.03	2
0.02 M total phosphate	7.03	71
0.02 M total phosphate	7.91	510
0.02 M total phosphate	8.60	1300
0.05 M total phosphate	8.60	1500
0.014 M total borate	9.0	4600
0.012 M total borate	9.5	12000

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[1] Work supported by a grant from the Atomic Energy Commission.

[2] L. H. Reyerson and S. Yuster, THIS JOURNAL, **56**, 1426 (1934); **57**, 779 (1935); see also L. H. Reyerson and B. Gillespie, *ibid.*, **57**, 2250 (1935); **58**, 282 (1936); and **59**, 901 (1937).

[3] R. P. Bell, *ibid.*, **57**, 778 (1935).

[4] J. B. Conant and G. W. Wheland, *ibid.*, **54**, 1212 (1932).

[5] W. K. McEwen, *ibid.*, **58**, 1124 (1936).